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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Readily Processable, Rigid Vinyl Chloride Polymer Compositions

We, THE DOW CHEMICAL COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, 5 State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to thermoplastic vinyl chloride polymer compositions having significantly improved processability. More particularly, the invention relates to rigid or essentially rigid thermoplastic compositions that are comprised of a vinyl chloride polymer blended with a chlorinated polyolefin and a polyolefin wax.

In accordance with the present invention, 20 readily processable rigid vinyl chloride polymer compositions are obtained by forming a composition comprising an intimate mixture of:

(1) a vinyl chloride polymer containing at least 80 weight per cent of polymerized vinyl chloride in the polymer molecule with the remainder, if any, being at least one monoethylenically unsaturated comonomer.

(2) between 0.1 and 50 parts by weight per 30 100 parts of vinyl chloride polymer of a chlorinated polyolefin, and

(3) between 0.1 and 3 parts by weight per 100 parts of vinyl chloride polymer of a polyolefin wax, having an average molecular weight of between 300 and 15,000.

These compositions, when employed in molten form in any conventional fabrication process, are essentially free from adhesion to the metal surfaces of the fabrication equipment. As a result, shaped articles are produced

40 having excellent surface characteristics and appearance, i.e., surfaces which are essentially free from undesirable ridges, grooves and other

irregularities. Further, use of such compositions provides significantly enhanced fabrication efficiency, particularly when extruding and blow-molding the same into articles such as bottles and the like. In addition to possessing excellent processability, the compositions of the present invention and shaped articles formed therefrom are characterized by tensile strength, tensile modulus, heat distortion properties and clarity which are comparable to conventionally prepared rigid thermoplastic vinyl chloride polymer compositions.

The vinyl chloride polymer included in the polymer blends may be any rigid or essentially rigid vinyl chloride homo-polymer or interpolymers of vinyl chloride with monomers such as vinyl esters or organic acids containing 1 to 18 carbon atoms, e.g., vinyl acetate, vinyl stearate, and so forth; vinylidene chloride; symmetrical dichloroethylene; acrylonitrile; methacrylonitrile; alkyl acrylate esters in which the alkyl group contains 1 to 8 carbon atoms, e.g., methyl acrylate and butyl acrylate; the corresponding alkyl methacrylate esters; dialkyl esters of dibasic organic acids in which the alkyl groups contain 1 to 8 carbon atoms, e.g., dibutyl fumarate and diethyl maleate.

The chlorinated polyolefins to be used according to the invention are those chlorination products of polymers and copolymers of monoolefins, e.g., ethylene, propylene, butene, isobutylene and mixtures thereof. Especially suitable are the chlorinated products of essentially linear and unbranched polyolefins such as chlorinated polyethylene and chlorinated copolymers of ethylene with butene or propylene, and more particularly, those essentially non-crystalline chlorinated products of essentially linear and unbranched polyolefins wherein the chlorine substituents are arranged predominantly in a random or uniform manner along the polymer molecule. The process by

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- which the starting polyolefins have been prepared, and the procedure used for chlorinating the same are, however, no critical to the present invention. It is only necessary that the 5 chlorinated products are present in the vinyl chloride polymer composition (in combination with the required amounts of the polyolefin wax) in amounts sufficient to provide between 0.1 part and 50 parts by weight of chlorinated 10 polyolefin per 100 parts of vinyl chloride polymer.
- It has been found that the utilization of up to about 50 parts, per 100 parts of vinyl chloride polymer, of a product obtained by 15 chlorinating essentially linear and unbranched polymer of non-aromatic hydrocarbon monoolefins of from 2 to 4 carbon atoms in aqueous suspension, to a total chlorine content of between 20 an 75, preferably 25 to 45 weight 20 per cent, while maintaining such polyolefin in an essentially noncrystalline form, provides significantly enhanced processability without adversely affecting the tensile strength or rigidity of the polymeric composition.
- 25 Amounts of these chlorinated products in excess of 50 parts by weight alters the processability of such polymer composition, however, to the extent that undesirable irregularities are often obtained on the surface of articles fabricated therefrom.
- 30 Further, it has been found that addition of such chlorinated products in amounts in excess of 50 parts by weight per 100 parts of vinyl chloride polymer, often reduces the clarity of 35 fabricated articles, e.g. blown bottles to the extent of providing opaqueness.
- The polyolefin waxes employed in the present invention are those polyolefin polymers and copolymers having an average molecular 40 weight of between 300 and 15,000 as determined by procedures such as described by Sperati et al, Journal of the American Chemical Society, 75, 6129 (1953). Particularly preferred materials, however, are those 45 polyethylene waxes having an average molecular weight of between 1500 and 5000. The polyolefin waxes are employed in concentrations between 0.1 to 3 parts per 100 parts of vinyl chloride polymer. Concentrations of 50 polyolefin waxes in excess of 3 parts per 100 parts of vinyl chloride polymer are generally unnecessary and may tend to deleteriously affect the physical properties, such as tensile strength, elongation and clarity of the vinyl 55 chloride polymer compositions and articles formed therefrom.
- The vinyl chloride polymer compositions of the invention may be formulated and prepared in any conventional manner, as by dry blending the polymeric ingredients and milling them at elevated temperatures of between 150 and 60 200° C. with conventionally employed compounding and milling rolls and the like apparatus. Such compositions are particularly useful 65 for the provision of molten or extruded articles
- or otherwise shaped or fabricated articles of the rigid, chemically resistant type such as pipes and tubing and blown bottles and the like articles.
- It is another embodiment of the present 70 invention that the impact strength of the rigid, readily processable vinyl chloride polymer compositions of the present invention may be significantly increased without reduction of other desirable properties, by the incorporation therein, by conventional means, of one or more other resinous impact strength modifiers which are compatible with vinyl chloride polymer compositions.
- In this regard, particularly good results are 75 obtained by the addition of from 1 to 25 parts by weight, and preferably between 18 and 22 parts by weight per 100 parts of the vinyl chloride polymer of one or more graft copolymers of styrene-acrylonitrile or styrene-isobutylene-acrylonitrile mixtures upon polybutadiene. Another useful impact strength modifier is the thermoplastic acrylic polymer available commercially as "Acryloid KM-227" (Registered Trademark) when used in the above preferred amounts. Compositions containing such impact modifying materials in the stated amounts have been found to be particularly useful for preparing 80 extrusion fabricated articles such as extrusion-blown molded bottles and the like. It is to be understood, however, that these and many other conventionally employed impact strength modifiers may be used in widely varying amounts, depending upon the properties desired, providing such materials remain compatible with the vinyl chloride polymer compositions described herein.
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- EXAMPLE 1.
- In each of a series of experiments the following specified ingredients were individually admixed in a Waring blender and extruded from a two-stage, one inch (2.54 cm) extruder operating about 44 rpm while employing a first stage cylinder temperature of about 350° F. (177° C.) and a second stage cylinder temperature of about 410° F. (210° C.). Individual rod-shaped test samples were obtained by extrusion through a single 0.275 x 1.25 inch (0.7 x 3.2 cm) cylindrical die.

The following Table I, illustrates the advantages of utilizing a chlorinated polyolefin and a polyethylene wax as a processing aid for polyvinyl chloride. The formulations tested contained the following specified ingredients:

5 100 parts by weight of a polyvinyl chloride having an absolute viscosity in 2 per cent o-dichlorobenzene solution at 120° C., of 1.90 to 2.05 cps;

10 2.5 parts per 100 parts of polyvinyl chloride of stabilizer "Mark X" (Registered Trademark) a commercially available alkyl tin mercaptide;

15 0 to 0.2 parts, per 100 parts of polyvinyl chloride, of a polyethylene wax having an average molecular weight of about 2000 and sold commercially as "Plaskon 6-A" (Registered Trademark) and

20 0 to 1.5 parts per 100 parts of polyvinyl chloride of a chlorinated polyethylene (CPE) obtained by: (1) forming an aqueous slurry comprising 4000 grams water and 200 grams of a polyethylene having an essentially linear and unbranched molecular structure containing less than about 1 methyl group per 100

methylene units in its molecule, a density of about 0.96, an average molecular weight of about 67,000, and which had been prepared using a catalyst composed of triisobutyl aluminum and titanium tetrachloride; (2) charging such aqueous slurry to a 1 $\frac{1}{2}$ gallon (5.65 liters) autoclave with 8 grams of calcium chloride, about 0.5 cc of a 70 per cent solution of tertiary butyl peroxide in butanol; (3) chlorinating the charge, as a first suspension chlorination step, under about 30 psi (gauge) (3 atmosphere) of chlorine pressure at a temperature of about 90° C. until a chlorine content of about 18 per cent was obtained, and (4) further chlorinating the charge in a second suspension chlorination step, at a temperature of about 126° C. until a total chlorine content of about 35 per cent was obtained. The chlorination product was then isolated by filtration, washed free of residual hydrochloric acid and dried. Such product was characterized by having a relative crystallinity of less than about 10 per cent, tensile strength of about 1400 psi (98 kg/sq cm) and a 100 per cent modulus of about 200 psi (14 kg/sq cm). 30
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TABLE I

Run No.	Composition			Processability		Extrusion Rate lbs/hr (kg/hr)
	CPE, Parts by wt.	PE Wax, Parts by wt.	Appearance of Extrudate Surface	Current Requirements (Amps) for Extrusion		
<u>For Comparison</u>						
1	—	—	Rough	12.2	7.6 (3.6)	
2	1.5	—	Rough	10.15	4.8 (2.2)	
3	—	0.2	Rough	9.4	1.8 (.81)	
<u>This Invention</u>						
4	1.5	0.2	Smooth	9.7	7.1 (3.2)	

Similar good results were obtained wherein the above described compositions additionally contained 20 parts by weight per 100 parts of polyvinyl chloride, of the following conventionally used polyvinyl chloride impact strength modifiers.

"Acryloid KM-227" (Registered Trademark) a commercially available thermoplastic acrylic polymer.

“Blendex 401” (Registered Trademark) a graft copolymer of styrene-acrylonitrile upon polybutadiene having essentially 49 weight per cent styrene, 21 weight per cent acrylonitrile and 30 weight per cent butadiene; or

EXAMPLE 2.
The following Table II illustrates the effects of the addition of the chlorinated polyethylene and polyethylene wax (as defined in Example 1) upon the physical properties of the following polyvinyl chloride compositions. These compositions were prepared and tested as previously described in Example 1.

TABLE II

Run No.	For Comparison	This Invention
Component	5 (Parts by Weight)	6
<u>PVC (having an absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120°C. of 1.90 to 2.05 cps)</u>		
PVC (having an absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120°C. of 1.90 to 2.05 cps)	100	100
"Blendex 401" (a graft copolymer of styrene-acrylonitrile upon polybutadiene)	20	20
Stabilizer "Mark X" (an alkyl tin mercaptide)	2.5	2.5
Chlorinated Polyethylene (as described in Example 1)	—	1.5
Polyethylene Wax (as described in Example 1)	—	0.5
<u>Physical Properties</u>		
Tensile Strength at Yield $\times 10^3$, psi (kg/sq. cm.)	7.6 (.53)	7.3 (.51)
Modulus at Yield $\times 10^3$, psi (kg/sq. cm.)	354 (24.8)	329 (23)
Heat Distortion Temperature, °C.	69	68.5

The above data illustrate that the addition of the described chlorinated polyethylene and polyethylene wax to the polyvinyl chloride

composition does not deleteriously effect the 5 physical properties of such compositions.

EXAMPLE 3.

The following Table III illustrates the effects produced by employing varying

amounts of a chlorinated polyethylene and a polyethylene wax. Each of the compositions contained the following specified ingredients.

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	Parts by Weight
Polyvinyl chloride (1.90 to 2.05 cps absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120°C.)	50
Polyvinyl chloride (1.6 to 1.8 cps absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120°C.)	50
Stabilizer "Mark X" (an alkyl tin mercaptide)	2.5
Impact Modifier "Blendex 401" (a graft copolymer of styrene-acrylonitrile upon polybutadiene)	20
Chlorinated Polyethylene (as generally described in Example 1 having from about 35 to 67 per cent chlorine)	1.5—35
Polyethylene Wax (as described in Example 1)	0.2—0.5

Similar good results were obtained using mixtures of (a) from 0.1 to 50 parts by weight per 100 parts of polyvinyl chloride of a chlorinated polyethylene prepared as essentially described in Example 1 having a chlorine content of from 20 to 75 weight per cent and (b) from 0.1 to 3 parts by weight per 100 parts of polyvinyl chloride of the herein described polyethylene wax. When using the stated amounts of a chlorinated polyethylene having a chlorine content of from 25 to 45 weight per

cent, a relative crystallinity of between 15 and 28 per cent when containing 25 weight per cent chlorine and a relative crystallinity of less than 10 per cent when containing 34 weight per cent of chemically combined chlorine, tensile strengths of at least 1300 pounds per square inch (91 kg/sq cm), elongations of at least 350 per cent and 100 per cent modulus of between 100 and 1000 pounds per square inch (7 and 70 kg/sq cm) were obtained.

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Composition

Run No.	Parts by Wt.	Per cent Chlorine	PE Wax. Parts by Wt.	Appearance of Extrudate Surface	Current Requirements (Amps) for Extrusion	Extrusion Rate lbs/hr (kg/hr)
7	1.5	35	0.2	Smooth	9.7	7.1 (3.2)
8	1.5	45	0.5	Smooth	9.3	2.1 (.95)
9	4.0	45	0.5	Smooth	9.4	3.5 (1.6)
10	8	45	0.5	Smooth	9.5	6.1 (2.8)
11	8	58	0.5	Smooth	9.4	4.2 (1.9)
12	8	67	0.5	Smooth	9.4	Not measured
13	12	48	0.5	Smooth	10.0	7.3 (3.3)
14	35	48	0.5	Smooth	10.3	8.1 (3.7)

EXAMPLE 4.
The following Table IV illustrates the effects of employing polyethylene wax of varying average molecular weight. Each of the

following compositions were individually prepared and extruded into test samples as hereinbefore described in Example 1.

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	Parts by Weight
Polyvinyl chloride (1.90 to 2.05 cps absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120°C.)	100
"Blender 401" (A graft copolymer of styrene-acrylonitrile upon polybutadiene)	20
Stabilizer "Mark X" (an alkyl tin mercaptide)	2.5
Chlorinated polyethylene (as described in Example 1)	2
Polyethylene wax (average molecular weight ranging from 1500 to 50,000)	0.75

TABLE IV

Run No.	P.E. Wax Avg. Mol. Wt.	Appearance of Extrudate Surface	Current Requirements (Amps) for Extrusion
<u>For Comparison</u>			
15	50,000	Rough	—
16	26,000	Rough	11.25
17	16,000	Rough	11.2
<u>This Invention</u>			
18	5,000	Smooth	9.85
19	2,000	Smooth	9.95
20	1,500	Smooth	9.75

- 10 The following Table V illustrates the effect of substituting various conventionally used lubricants for the chlorinated polyethylene and

polyethylene wax. The following compositions were prepared and tested as described in Example 1.

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	Parts by Weight
Polyvinyl chloride (1.90 to 2.05 cps absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120°C.)	100
"Blendex 401" (A graft copolymer of styrene-acrylonitrile upon polybutadiene)	20
Stabilizer "Mark X" (an alkyl tin mercaptide)	2.5
Processing aid	2.0

TABLE V

Run No.	Processing Aid	Appearance of Extrudate Surface	Current Requirements (Amps) for Extrusion
<u>For Comparison</u>			
21	Calcium Stearate	Rough	11
22	Stearic Acid	Rough	10.75
23	Mineral Oil	Rough	11.15
24	1.5 parts glycerol (monostearate plus 0.5 parts polyethylene wax of avg. mol. wt. of 2000)	Rough	9.7
<u>This Invention</u>			
	1.5 parts CPE plus 0.5 parts polyethylene wax of an avg. mol. wt. of 2000	Smooth	9.65

EXAMPLE 6.

The following Table VI illustrates the effect of using either of two commercially available, high molecular weight chlorinated polyethylenes; "Plaskon" Polymer Modifier 101

and "Plaskon" Polymer Modifier 102 as the chlorinated polyethylene ingredient. The following compositions were prepared and tested as described in Example I.

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	Parts by Weight
Polyvinyl chloride (1.90 to 2.05 cps absolute viscosity in 2 per cent ortho-dichlorobenzene solution at 120 °C.)	50
Polyvinyl chloride (1.6 to 1.8 cps absolute viscosity in a 2 per cent ortho-dichlorobenzene solution at 120 °C.)	50
Stabilizer "Mark X" (an alkyl tin mercaptide)	50
Impact Modifier "Blendex 401" (a graft copolymer of styrene-acrylonitrile on polybutadiene)	20
Polyethylene wax (having an average mol. wt. of 2000)	0.5
"Plaskon" Polymer Modifier 101 (a high molecular weight chlorinated polyethylene in the form of a dry, colorless powder having a chlorine content of about 46 per cent)	1—2
"Plaskon" Polymer Modifier 102 (a high molecular weight chlorinated polyethylene in the form of a dry, colorless powder having a chlorine content of about 40 per cent)	1—2

TABLE VI

Run No.	Type	Composition (pts. by wt.) CPE	Amount	Appearance of Extrudate Sur- face	Processability Requirements (Amps) for Extrusion
This Invention					
26	"Plaskon" 101	1		Smooth	10
27	"Plaskon" 101	2		Smooth	9.8
28	"Plaskon" 102	1		Smooth	9.5
29	"Plaskon" 102	2		Smooth	9.5

EXAMPLE 7.

In each of a series of experiments the following specified ingredients were individually dry-blended under high-speed agitation. Each blend was then individually fed directly to and extruded from a two-stage, 2.5 inch

(6.36 cm) vented extruder operating at temperatures of from about 300 to 410° F. (150 to 210° C.). Each extrudate was then separately used to produce a plurality of blown bottles.

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Parts by Weight
Polyvinyl chloride (1.90 to 2.05 cps absolute viscosity in a 2 per cent ortho-dichlorobenzene solution at 120°C.)
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Polyvinyl chloride (1.6 to 1.8 cps absolute viscosity in a 2 per cent ortho-dichlorobenzene solution at 120°C.)
50
Stabilizer "Mark X" (an alkyl tin mercaptide)
2.5
Impact Modifier "Blendex 401" (a graft copolymer of styrene-acrylonitrile on polybutadiene)
20
Polyethylene wax (as described in Example 1)
0.1-1
Chlorinated polyethylene (as described in Example 1)
0.2

- Blown bottles prepared as described herein from compositions containing from 0.1 to 2 parts by weight of the described chlorinated polyethylene and 0.1 to 1 part by weight of the described polyethylene wax were easily processed and were characterized by excellent surface smoothness, gloss and clarity and, in addition, were completely free from undesirable discoloration. In comparison, however, blown bottles as identically prepared from compositions absent the chlorinated polyethylene were, in all instances, characterized by surface irregularities and discoloration along the weld line of the parison.

WHAT WE CLAIM IS:—

1. A composition comprising an intimate mixture of (1) a vinyl chloride polymer containing at least 80 weight per cent of polymerized vinyl chloride in the polymer molecule with the remainder, if any, being at least one monoethylenically unsaturated comonomer, (2) from 0.1 to 50 parts by weight per 100 parts of the vinyl chloride polymer of a chlorinated polyolefin, and (3) from 0.1 to 3 parts by weight per 100 parts of said vinyl chloride polymer of a polyolefin wax having an average molecular weight of between 300 and 15,000.

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2. A composition as claimed in claim 1, wherein the vinyl chloride polymer is poly-vinyl chloride. 25
3. A composition as claimed in claims 1 and 2 wherein the chlorinated polyolefin is the product obtained by chlorinating an essentially linear and unbranched polyolefin of a non-aromatic hydrocarbon olefin of from 2 to 4 carbon atoms to a combined chlorine content of from 20 to 75 per cent by weight while the polyolefin is maintained in aqueous suspension in a substantially non-crystalline form. 30
4. A composition as claimed in claims 1 or 2 wherein the chlorinated polyolefin is polyethylene containing from 25 to 45 weight per cent of chemically combined chlorine. 35
5. A composition as claimed in any one of claims 1 to 4 wherein the polyolefin wax is polyethylene wax having an average molecular weight between 1500 and 5000. 40
6. A composition as claimed in any one of claims 1 to 5 containing in addition thereto, from about 1 to 25 parts by weight per 100 parts of the vinyl chloride polymer of a resinous impact strength modifier which is compatible with the composition.
7. A composition as claimed in claim 6 wherein the resinous impact strength modifier is a graft copolymer of a styrene-acrylonitrile mixture upon polybutadiene.
8. A vinyl chloride polymer composition containing a chlorinated polyolefin and a polyolefin wax having a molecular weight of from 300 to 15,000 substantially as hereinbefore described with reference to the specific Examples.
9. An essentially rigid, thermoplastic, shaped article having smooth surfaces and prepared from an intimate fusion blend of the composition of any one of claims 1 to 8.
10. The article of claim 9 which is an extrusion-blow molded bottle.

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